

UNCLASSIFIED

AD - 410384

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

410384

CATALOGED BY DDC

AS AD No. ~~410384~~

11-68-4-3

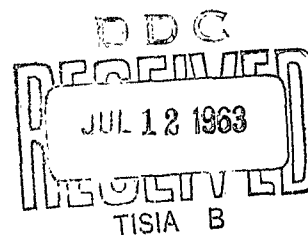
Technical Report No. 0309

EVALUATION OF A SERIES OF THERMOPLASTIC
POLYURETHANE ELASTOMERS

Reported by: James C. Eaton, Jr.

Supervised by: Carl A. Nielson

June 1963



U. S. ARMY PROSTHETICS RESEARCH LABORATORY
WALTER REED ARMY MEDICAL CENTER
WASHINGTON 12, D. C.

T.R. No. 6309*

Project: CX59-01-001-04

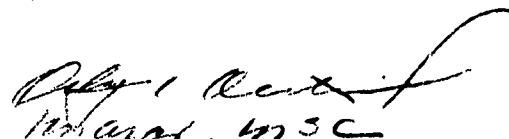
Date Started: January 1963

Date Completed: June 1963

Recommend Approval:


Acting Scientific Director

Approved:


Director

*Qualified requesters may obtain copies of this report from ASTIA.

T.R. No. 6309

A B S T R A C T

Physical properties and the resistance to attack by ultraviolet radiation and moisture have been determined for a series of thermoplastic polyester-urethane materials. Results of preliminary investigations into the manufacture of polyurethane coated cosmetic gloves with superior surface characteristics are reported.

I. INTRODUCTION

Polyurethane elastomers with their excellent abrasion resistance and extensibility, appear useful as a cosmetic glove material and in other prosthetic uses. Most of these elastomers require curing agents and have limited pot life, hence limited application to small scale batch operations, such as the manufacture of cosmetic gloves.^{1/} The Estane materials, a series of poly (ester-urethane) elastomers which are believed to be essentially linear polymers, behave as typical thermoplastics. These materials are fully cured and can be converted into end products by milling, calendering, extrusion, molding, and solvent casting.^{2/} These are supplied in a series of three resins of varying moduli accompanied by three homologues modified for improved hydrolytic stability. They are:

1. Estane 5740X1 (Std. Resin)
2. Estane 5740X1-HS (Improved hydrolytic stability)
3. Estane 5740X2 (Lowest modulus)
4. Estane 5740X2-HS
5. Estane 5740X7 (Highest modulus)
6. Estane 5740X7-HS

They are available in amber-colored, clear 3/16" cubular granules.^{3/}

II. PREPARATION OF SAMPLES

Each of the Estane materials was dissolved in the appropriate solvent. The 5740X2 and its hydrolytically stable homologue are soluble in methyl ethyl ketone (MEK) but the other four resins required more powerful solvents. They were dissolved in tetrahydrofuran (THF). The solutions contained between 10 and 15 per cent solids. Resin and solvent were weighed into a cylindrical metal can and rolled overnight to achieve solution.^{3/}

In order to cast bubble-free films it was necessary to deaerate the solutions under vacuum. Films were cast on polished metal plates and drawn down to uniform thickness with a knife having a micrometer adjustment. Initial drying was at room temperature for four to six hours, followed by overnight drying at 47°C. and four to six hours at 60°C. The films prepared in this manner were clear and bubble-free and ranged in thickness from seven to twelve mils. It was not necessary to use a mold release agent; although it was found that films released more readily from a chromed steel plate than from one of polished aluminum.

III. TESTING PROCEDURES

Films prepared as described above were cut into test samples and the following tests were performed in the manner indicated.^{4/}

1. Tensile Testing: Tensile strength, ultimate elongation (at break) modulus (tensile stress) and data for the stress-strain curves were taken

Footnotes 1 - 3 listed under References.

according to ASTM D412-51T, "Tension Testing of Vulcanized Rubber" using the Instron tension testing machine.

2. Tear Resistance: Tear resistance was taken according to ASTM D524-54, "Tear Resistance of Vulcanized Rubber" with the Instron machine.

3. Low Temperature Stiffness: This was taken according to ASTM D747-53T, "Stiffness in Flexure of Plastics" using the Tinius-Olsen stiffness tester in a refrigerated atmosphere at 10° intervals from -40°C to + 10°C.

4. Stain Resistance: This was taken using the techniques of Mr. James T. Hill in APRL Tech. Reports 6202, 5904, 5903 and 5838. The acrylate cleaning solution (9 pts. methanol to 1 pt. MEK) was used.

5. Ultraviolet Degradation: Samples were subjected to ultraviolet light (ASTM D520-57T) for varying periods of time. Color readings were taken using the Gardner color difference meter with the one inch opening and condensing lenses. The standard white tile with an Rd value of 88.9 was used. Tensile properties were taken after 10 days as described above.

6. Hydrolytic Stability: The procedure followed was similar to that of ASTM D1239-55 "Resistance of Plastic Films to Extraction by Chemicals." Three samples of each material approximately 6 inches by 1 inch were cut out and weighed on a semi-micro balance. The thickness of each sample was measured at a particular point. The samples were then suspended in distilled water at 60± 1°C. for 28 days, after which time they were removed, wiped dry, weighed and measured again. Tensile test specimens were cut from each sample and tensile properties were determined as described above.

The results of these tests are to be found in the tabulations and graphs in the Appendix attached to this report. A sketch of the hydrolytic stability apparatus will also be found in the Appendix.

IV. DISCUSSION OF RESULTS

As can be seen from the data of Table I in the Appendix, the Estane materials have a tensile strength of up to five times that of a typical vinyl, such as is used in cosmetic glove formulations. The stain resistance of the two higher modulus grades (X1 and X7) is also much greater than that obtained from plasticized vinyl compositions. The flexibility and extensibility (as measured by the "modulus") of these two resins and their more hydrolytically stable homologues are inferior to those of vinyls. The X2 and X2-H3 materials retain adequate tensile and tear strength qualities and have in addition excellent flexibility and extensibility. But in this case stain resistance is sacrificed. These

latter two materials are also most adversely affected by both ultraviolet light exposure and immersion in water at 60°C.

Hydrolytic stability tests indicate that these materials (with the exceptions of X2 and X2-HS) retain useful physical properties even after 20 days immersion in distilled water at 60°F. This might indicate applications to internal prosthesis. As was to be expected, the HS grades were superior to the standard in this respect, but the difference in hydrolytic stability between the different standard grades of these materials was just as great as the difference between the standard and hydrolytically improved materials of the same grade. Estane 5740X2 was almost completely disintegrated in the hydrolytic stability test. The samples lost so much strength that they tore at the point of suspension under their own weight.

Exposure to ultraviolet radiation had the effect of appreciably darkening and hardening the films of all six Estane materials, most apparent in the X-2 grades; least so in the X-7 grades. The hardening, or embrittling effect was evident in an increase in modulus and a decrease in ultimate strength of the materials. It was also noted that the specimens cracked upon being subject to strain. This cracking, which showed up on the stress-strain curve as a flat portion of increased strain without any corresponding increase in stress, occurred only on that side of the film which faced the UV lamp. This would indicate that penetration was not very deep. It can be surmised that darkening of the film under UV exposure effectively blocks out further penetrations of the rays, a protective mechanism analogous to that of human skin tissue.

The X-2 grade darkened the most under UV exposure and the X7 darkened the least. It should be noted, however, that the X7 was the darkest film originally and the X2 the lightest. The X7 and the X7-HS material showed the least evidence of surface cracking under strain, both visually and in the stress-strain curve.

The color data of Table V offer only a comparative idea of the effect of UV on color, since it was not possible to control sample thickness so as to have equal samples of each material. In Figure II in the back of the report the percentage increase in "b" value, a comparative measure of yellowness obtained from measurements upon a Gardner-Hunter Color Difference Meter, are plotted against days exposure to UV radiation. For each of the Estane materials this gives a better picture of the varying degrees of degradation to be expected from these materials when they are exposed to sunlight.

From the plots of Figure IV it is apparent that the three grades of Estane materials that have been altered for improved hydrolytic stability show a similarity in their rates of UV induced degradation, forming a "family" of curves of similar shape and essentially equal slopes in the

linear portion of the curve. This similarity of curves is displayed to a lesser extent by the standard forms of these materials, with the 5740X2 leveling off at about 200 per cent of original "b" value (not shown on the curve).

The flexibility-at-low temperature data of Table VI are plotted in Figure IV. As compared to vinyl glove compositions, the Estanes range from extraordinarily flexible for the X-2 material to very stiff for the X-7 material. The Estane 5740X1 material is comparatively stiff at temperatures just below room temperature, but the stiffness does not increase as rapidly with decreasing temperature as is the case with plasticized vinyls^{5/}.

V. ESTANE MATERIALS AS COATINGS FOR COSMETIC GLOVES

Because those Estane materials which have the most desirable surface properties - abrasion resistance and stain resistance - are also the most inflexible and offer the most resistance to extension, it was felt that they could best be used as outer coatings for cosmetic gloves having a substrate of flexible vinyl or acrylate.

1. Vinyl Substrate. A vinyl plastisol was chosen for flexibility, designated E201-23-3.^{5/}

Geon 135	PVC co-polymer resin	550
Flexol Z	- 80 di-ethyl hexyl azelate	425
Ch201	-chelating agent	3
G-62	Stabilizer - epoxy	12
BC-30	Stabilizer - barium-cadmium	15

A cylindrical film of vinyl cast from this plastisol was wiped clean of surface plasticizer with a cloth saturated with methanol and dried. The cylinder was then weighted with sand and dipped in a 10 per cent solution of Estane 5740X7 in THF. A variable speed dip coater, ascending at approximately one inch per minute was used for this operation. The coating was dried at room temperature for 30 minutes and overnight at 47°C. The thickness of the coating was approximately one mil.

The vinyl film shrank noticeably in the area where the coating was deposited. This can be caused by either a shrinkage of the vinyl due to extraction of plasticizer by the solvent^{5/} or a shrinkage of the Estane coating, or by a combination of both. In any case the shrinkage presents a problem in the manufacture of cosmetic gloves in this manner.

The stain resistance of the coated film, using standard vinyl cleaning solution, equal parts of MEK, isopropanol and trichloroethylene, was 95%, as compared to 45% for the original film. The other physical properties were unchanged. The peel strength of the coating measured at

20 in/min. was 3.5 lbs/in. Unfortunately, the Estane coating imparted a high gloss to the film and when a cosmetic glove was dip-coated in this manner it lost its skin-like appearance and texture. It was evident that the Estane coating in order to be applicable to cosmetic gloves, would have to be applied to the surface of a glove mold so as to pick up the details of the skin. It was found impossible to perform the vacuum deaeration necessary to a homogeneous deposition in a slush mold without building up a film many times thicker at the top of the wrist than at the palm and fingers. The idea of a slush-molded vinyl substrate with Estane coating was temporarily set aside in favor of a dip molded acrylate terpolymer substrate.

2. Acrylate Substrate - A film of Estane 5740X7 was deposited on an epoxy dipping mold and after drying was found to be quite easily removable, much more readily than from a metallic mold.

The acrylate chosen for the substrate was a terpolymer of butyl acrylate, 2-ethyl hexyl acrylate and methacrylamide^{6/}. The procedure for making gloves was as follows: First the mold was dipped in Estane 5740X7 using the variable speed dip coater at approximately 1 inch per minute. This coat was allowed to dry at room temperature for two hours, followed by a second dip in the X7 material. After an additional two hours drying the mold was dipped in a 10% solution of Estane 5740X2 in MEK. This intermediate coating of low modulus polyurethane elastomer made for better adhesion between the acrylate and urethane layers. After two hours drying at room temperature, the Estane deposition was dried overnight at 47°C.

The standard fabrication procedure for acrylate cosmetic gloves was followed in the deposition of the acrylate substrate^{7/}.

1. Immerse Estane coated glove mold in coagulant and allow excess to drip off.
2. Immerse in BA/2-EHA/MAA latex. Remove immediately and invert.
3. Immerse a second time in coagulant and allow excess to drip off.
4. Immerse in BA/2-EHA/MAA latex and dwell for two minutes.
5. Leach wet film for two hours in warm water.
6. Dry in oven at 60°C, until deposited film becomes clear.
7. Remove glove from mold.

The gloves prepared in this manner had a stain resistance of 78% as compared to the dilaminar acrylate glove's 65%^{7/}. The gloves, however, were smaller than the No. 44 hand. This is probably caused by a combination

of the shrinkage of the urethane and acrylate, and the shrinkage inherent in the method of making the molds. It can be corrected by using a larger sized mold. There was some evidence of local non-adhesion between the layers. Another disadvantage of the dipping technique is the accumulation of polyurethane at the fingertips.

VI. FUTURE WORK

1. Dilaminar Cosmetic Gloves

Work will be continued on both the dilaminar gloves discussed herein - the vinyl substrate and the acrylate substrate. It may be possible to process the urethane coating in the vinyl slush mold in vacuum, thus eliminating excessive coating build-up at the wrist. An epoxy slush mold has been prepared so that urethane coatings can release more readily.

2. Other Processing Methods

Equipment for milling and compression molding of thermoplastic elastomers is soon to be available and at that time procedures for molding gloves from the Estane materials will be investigated.

VII. CONCLUSIONS

1. The Estane polyester urethane materials offer physical and chemical properties which may find use in cosmetic gloves. As is usual among polymeric materials, the flexible materials show the least resistance to staining while the less flexible ones have outstanding stain resistance. And again a solution must be found either with a monolaminar glove of compromised stain resistance and flexibility, or alternatively by employing more expensive dilaminar techniques in the manufacture of cosmetic gloves.

In the case of the dilaminar glove more work is necessary to improve adhesion between layers and to eliminate build-up of coating at the fingertips. In order to manufacture a monolaminar glove from these materials, some method other than dip coating must be devised. The dipping process must be repeated several times and the material must be dried between successive dips. Other disadvantages of the dipping technique are the accumulation of excess material at the extremities and the formation of bubbles of entrapped air between the layers, both of which detract from the appearance of the cosmetic glove.

Table I - Summary of Physical Data

Estimate	5740X1		5740X2		5740X7	
	Reg	HS	Reg	HS	Reg	HS
Tensile Strength, psi	7,300	9,470	4,100	1,680	8,000	9,440
Ultimate Elongations %	510	360	750	610	440	515
Modulus - 100%	570	500	210	135	1,400	1,270
Modulus - 300%	1,500	1,300	290	225	3,870	3,940
Tear strength, pli	375	401	225	160	353	369
Stain Resistance %	82	70	61	66	83	85

PERCENT CHANGE AFTER 23 DA. WATER IMMERSION AT 60°C

Weight	+2.5	+5.5	+15.3	+49.7	+31.1	+1.8
Tensile Strength	-34	-42	-98	-64	-47	-20
Elongation	+36	-3	-78	+39	+7	+5
100% Modulus	-6	+15	-56	-31	+16	+8
300% Modulus	-42	-7		-60	-32	-28

PERCENT CHANGE AFTER 10 DA. ULTRA-VIOLET EXPOSURE

Tensile strength	-51	-47	-56	-55	+13	-13
Elongation	-23	-39	-21	-20	-18	-18
100% Modulus	+43	+52	+33	+45	+63	+40
300% Modulus	+37	+20	+38	+32	+79	+38
"b" Value	+60	+59	+178	+77	+40	+44

Table II Stress-Strain Data
Stress in psi at Elongation Indicated

Elongation	50	100	200	300	400	500	600	700	Break	
									Elong	Stress
Estane										
5740X1	550	670	930	1600	4315	7215	-	-	510	7380
5740X1-HS	450	600	890	1330	3180	6610	8500	-	660	9470
5740X2	100	210	230	290	415	730	1360	2640	750	4100
5740X2-HS	140	185	205	225	330	570	1420	-	610	1680
5740X7	1110	1400	2150	3870	6400	-	-	-	440	8000
5740X7-HS	1000	1270	2110	3940	6150	9120	-	-	515	9440

Table III Effect of 28 Days Immersion in Water
at 60°C Upon Stress-Strain Data

Stress in psi at Elongation Indicated

Elongation	50	100	200	300	400	500	600	700	800	Break	
										Elong	Stress
Estane											
5740X1	517	630	700	933	1150	1387	1640	1935	-	697	1920
5740X1-HS	530	690	910	1230	1950	3290	5250	-	-	610	5450
5740X2	70	92	102	-	-	-	-	-	-	167	98
5740X2-HS	50	72	78	89	110	148	206	316	454	850	608
5740X7	1200	1510	1880	2530	3540	-	-	-	-	470	4260
5740X7-HS	1110	1370	1050	2050	4660	6510	-	-	-	540	7540

Table IV Effect of 10 Days Exposure to Ultra-Violet
Radiations Upon Stress-Strain Data

Stress in psi at Elongation Indicated

Elongation	50	100	200	300	400	500	Break	
							Elong	Stress
Estane								
5740X1	680	930	1450	2190	-	-	370	3630
5740X1-HS	700	920	1430	2610	4980	-	400	4980
5740X2	170	247	340	400	537	967	593	1793
5740X2-HS	175	270	355	410	510	-	450	760
5740X7	1500	2120	3440	5590	-	-	350	9030
5740X7-HS	1800	1700	2030	5410	7630	-	420	8200

Table V Color Degradation with Ultra-Violet Exposure

"b" Value after No. of Days Indicated

Time, days	0	1	2	3	4	6	8	10	14
Estane									
5740X1	14.3	17.0*	19.5*	21.4	23.1*	25.8	27.3*	28.4	30.1
5740X1-HS	17.0	21.3	23.3*	24.3*	25.1	26.2	26.6	27.1*	28.2
5740X2	9.0	15.6	18.7	20.9	22.2*	24.4*	25.1	27.2	28.6
5740X2-HS	10.7	23.0	24.7	25.1	27.0	27.6*	28.8*	29.5	30.5
5740X7	19.9	21.5	23.6	24.7	25.1	26.2*	27.1*	27.9	29.3
5740X7-HS	10.5	19.0	20.7*	21.2*	21.7	22.8	23.3	22.7*	24.1

(*) Data graphically interpolated

Note: "b" value is a comparative measure of yellowness.

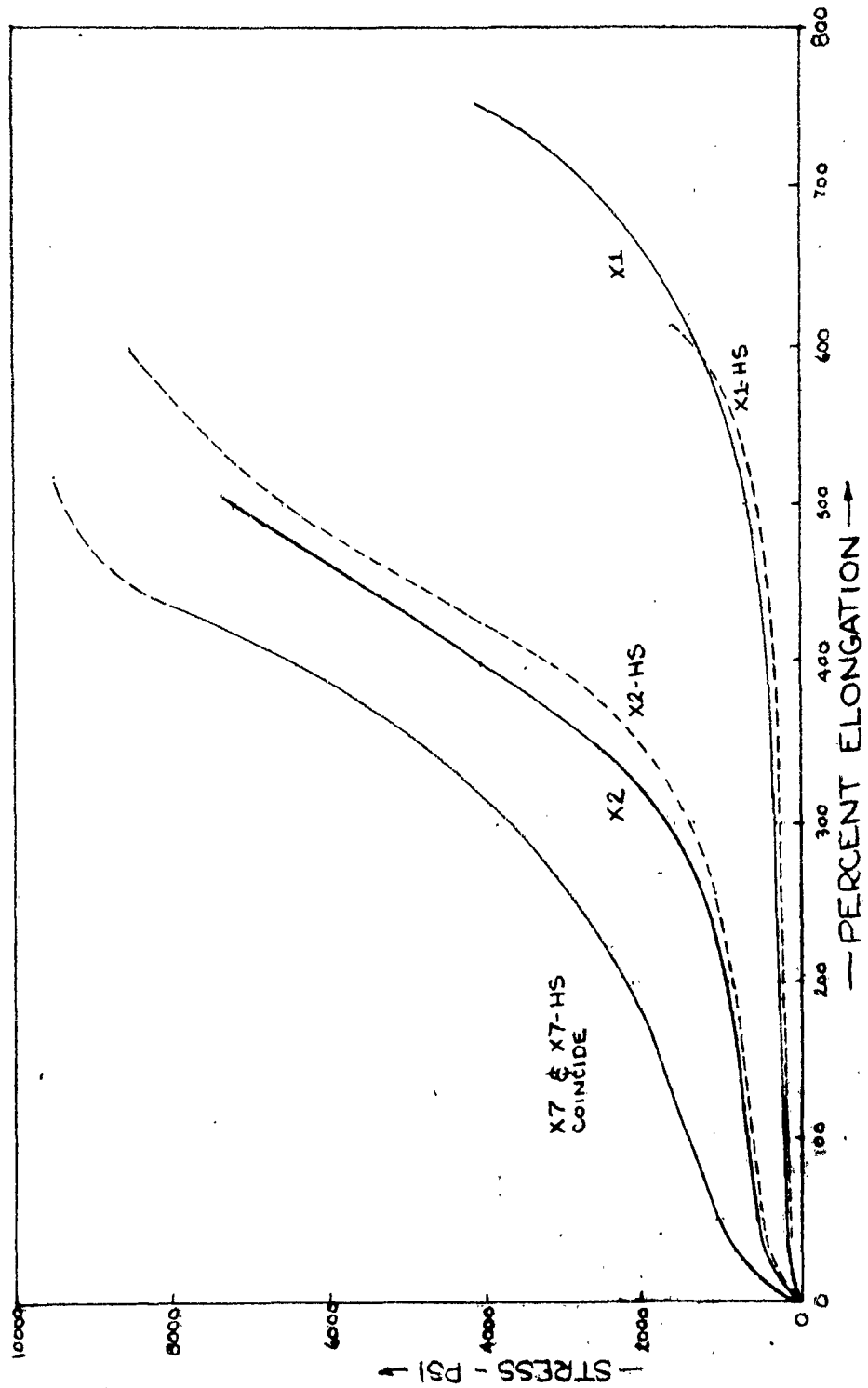
Table VI Flexibility at Low Temperatures

Stiffness in flexure, psi, at Temperature Indicated

	-40°C	-30°C	-20°C	-10°C	0°C	+10°C
Ethane						
5740X1	15,000	11,000	4,200	2,300	2,300	1,400
5740X1-HS	20,500	13,500	4,000	4,600	3,000	2,500
5740X2	11,700	1,500	1,070	1,025	-	990
5740X2-HS	41,000	2,300	730	470	-	470
5740X7	100,000	30,500	30,000	12,000	6,300	3,300
5740X7-HS	35,000	45,000	21,000	9,600	5,200	-

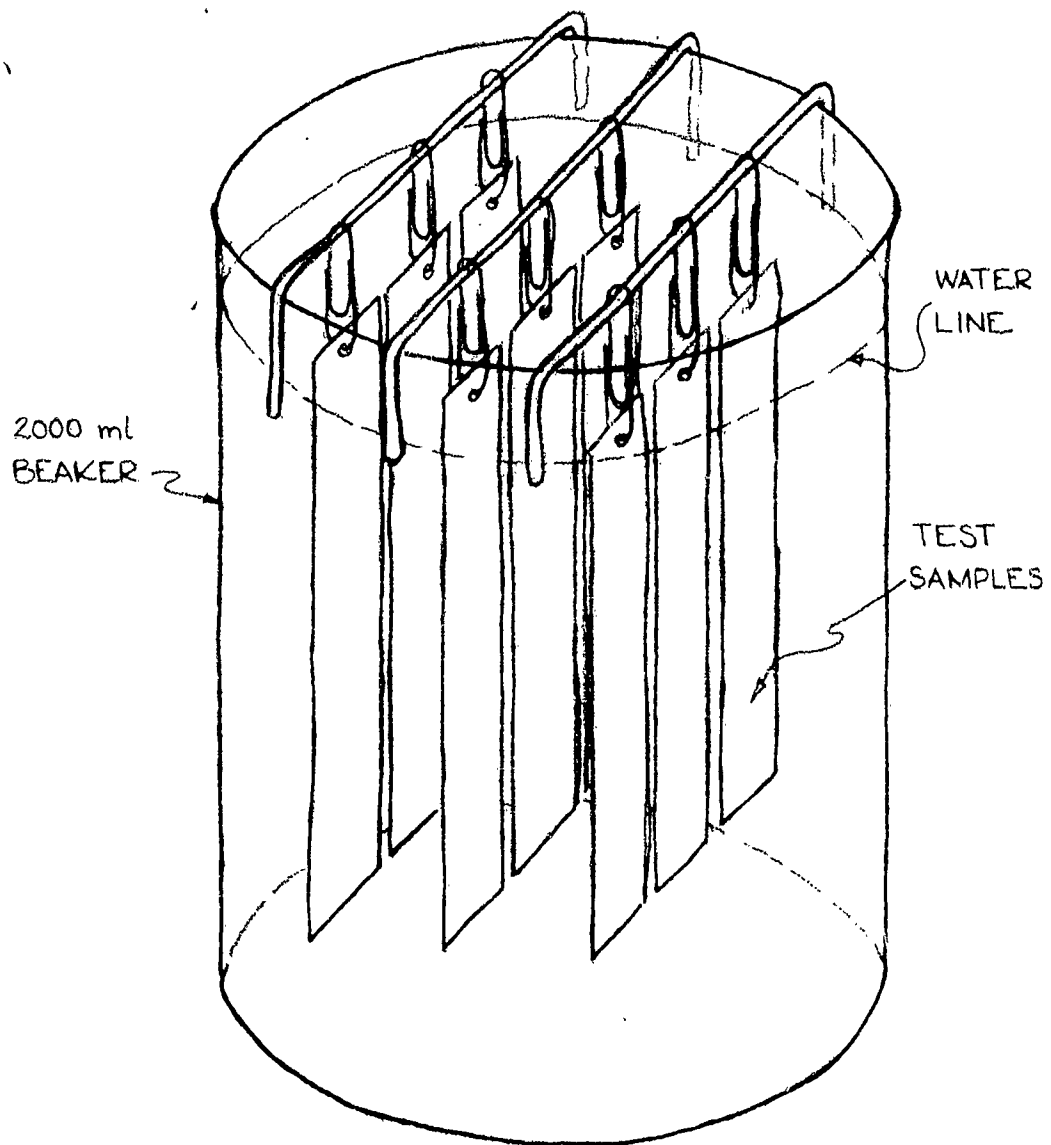
References

1. Eaton, James C., Jr., "Evaluation of Adiprene L-100 Urethane Rubber as a Cosmetic Glove Material", APRL Technical Report 6302, January, 1963.
2. Bulletin, "Estane Polyurethane Materials", Service Bulletin G-13, B. F. Goodrich Chemical Co., Revised July, 1960.
3. Communication, James F. Smith, B. F. Goodrich Chemical Co., Avon Lake, Ohio, January 4, 1963.
4. ASTM, "Standards" Part 9 "Plastics, Electrical Insulation, Rubber Carbon Black", 1958, American Society for Testing Materials, Philadelphia, Pa.
5. Eaton, James C., Jr., "Poly (vinyl chloride) Copolymer Resin Geon 135 in Plastisol Formulations for Cosmetic Glove, APRL Technical Report 6214, August, 1962.
6. Nelson, Joshua, "Physical Evaluation of 37/10.5/2.5, BA/2-EHA/MAD Elastomer", APRL Technical Report 6207, March, 1962.
7. Winer, Allen, "Fabrication of an Improved Acrylate Cosmetic Glove Composite", APRL Technical Report 6303, February, 1963.
8. APRL Research Notebook No. 201, pp 93-137.



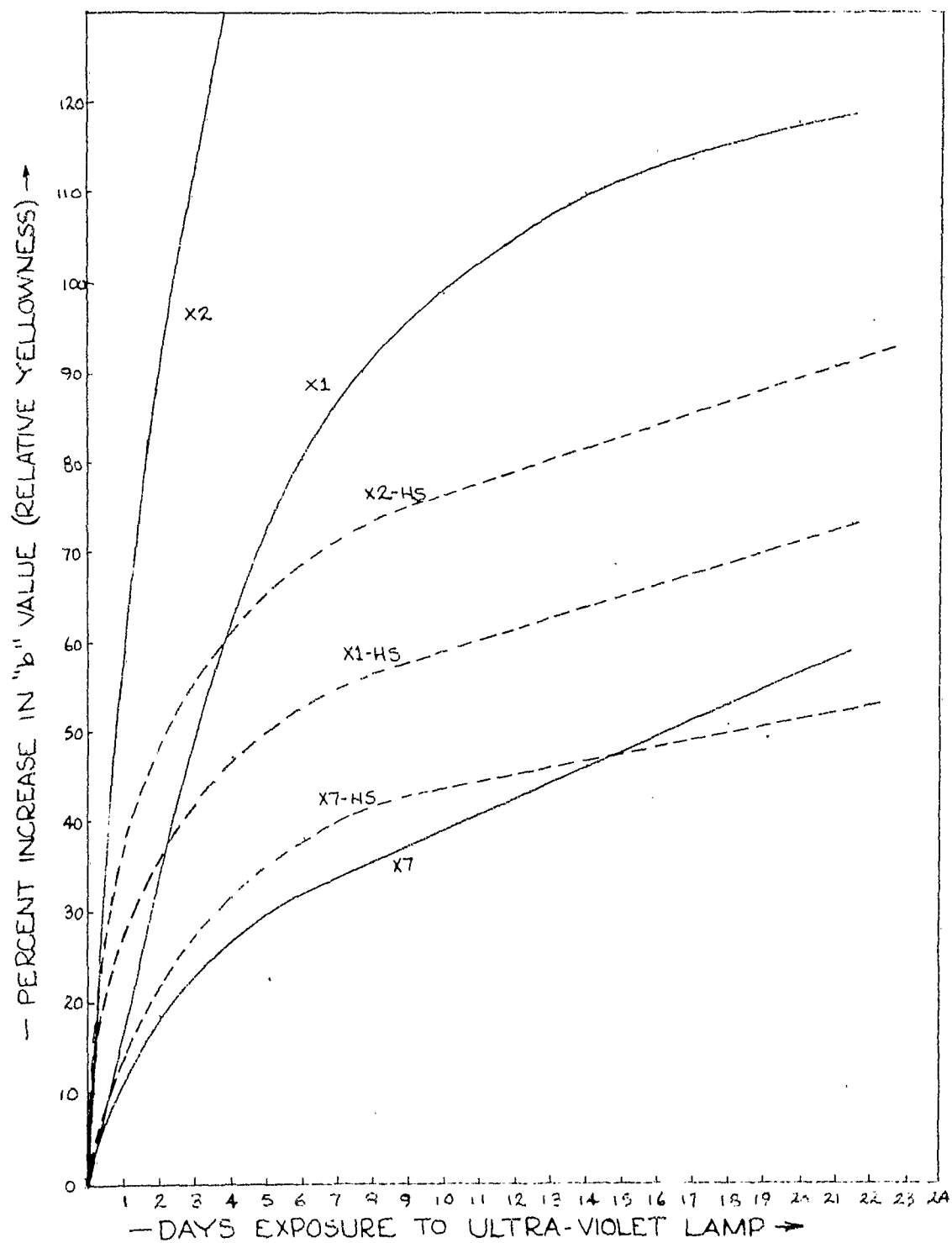
T.R. NO. 6309 FIG 1 - STRESS-STRAIN RELATIONSHIPS FOR
ESTANE POLYURETHANE MATERIALS

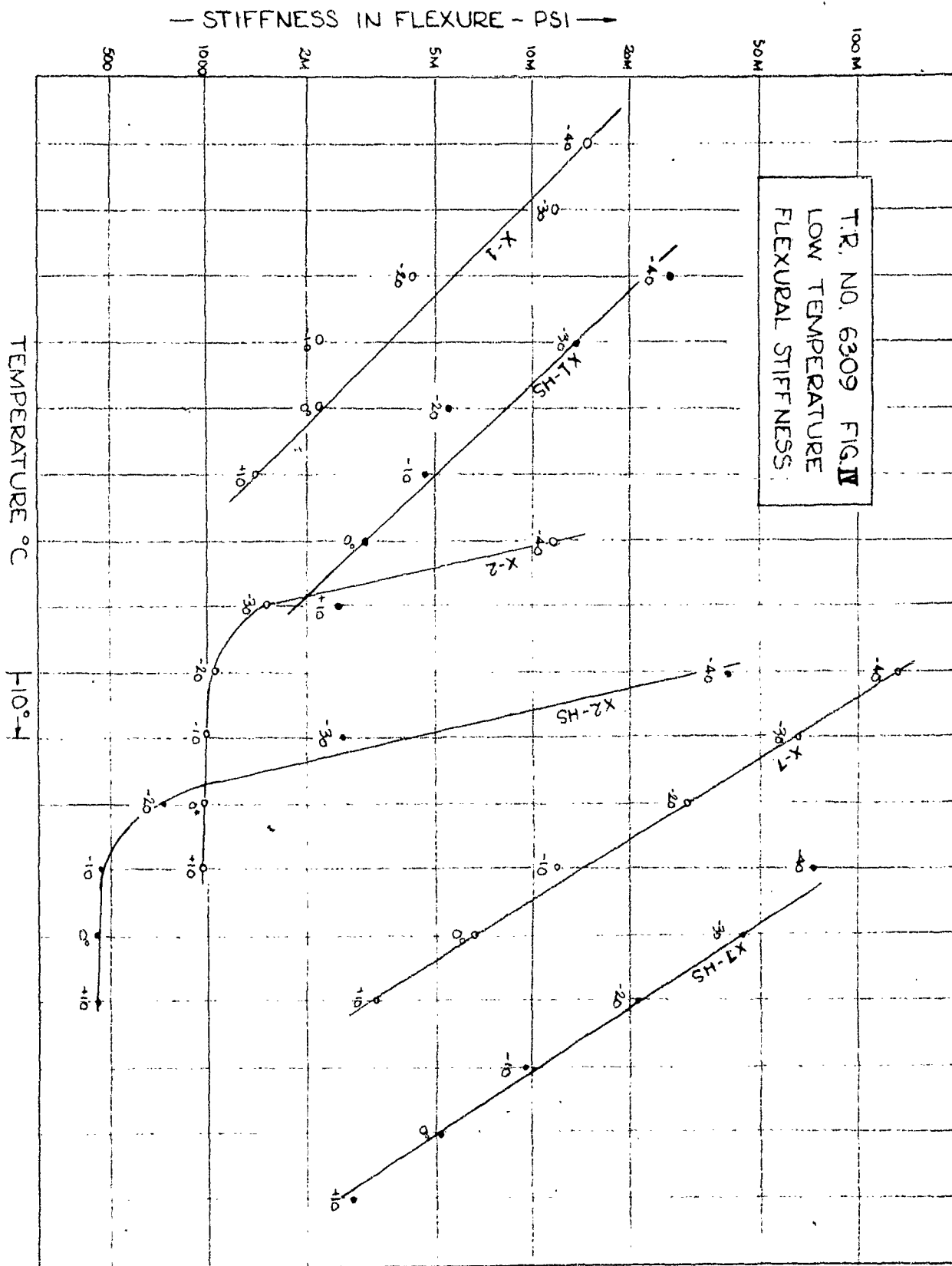
T.R. 6309 FIG II



HYDROLYTIC STABILITY DETERMINATION APPARATUS

T.R. 6309 FIG III - DEGRADATION OF COLOR OF ESTANE POLYURETHANE MATERIALS UNDER ULTRA-VIOLET LAMP





<p>ABSTRACT CARD</p> <p>TITLE: Evaluation of a Series of Thermoplastic Polyurethane Elastomers</p> <p>AUTHOR(S): James C. Eaton, Jr.</p> <p>AGENCY: USA Prosthetics Res. Lab.</p> <p>Walter Reed AMC, Washington 12, D. C.</p> <p>TECH. RPT. 6309</p> <p>Project 6X59-01-001-04</p> <p>ABSTRACT: Physical properties and the resistance to attack by ultraviolet radiation and moisture have been determined for a series of thermoplastic polyester-urethane materials. Results of preliminary investigations into the manufacture of polyurethane coated cosmetic gloves with superior surface characteristics are reported.</p> <p>WRAMC FORM 0183 (ONE TIME) 15 MAY 1961</p>	<p>ABSTRACT CARD</p> <p>TITLE: Evaluation of a Series of Thermoplastic Polyurethane Elastomers</p> <p>AUTHOR(S): James C. Eaton, Jr.</p> <p>AGENCY: USA Prosthetics Res. Lab.</p> <p>Walter Reed AMC, Washington 12, D. C.</p> <p>TECH. RPT. 6309</p> <p>Project 6X59-01-001-04</p> <p>ABSTRACT: Physical properties and the resistance to attack by ultraviolet radiation and moisture have been determined for a series of thermoplastic polyester-urethane materials. Results of preliminary investigations into the manufacture of polyurethane coated cosmetic gloves with superior surface characteristics are reported.</p> <p>WRAMC FORM 0183 (ONE TIME) 15 MAY 1961</p>
<p>ABSTRACT CARD</p> <p>TITLE: Evaluation of a Series of Thermoplastic Polyurethane Elastomers</p> <p>AUTHOR(S): James C. Eaton, Jr.</p> <p>AGENCY: USA Prosthetics Res. Lab.</p> <p>Walter Reed AMC, Washington 12, D. C.</p> <p>TECH. RPT. 6309</p> <p>Project 6X59-01-001-04</p> <p>ABSTRACT: Physical properties and the resistance to attack by ultraviolet radiation and moisture have been determined for a series of thermoplastic polyester-urethane materials. Results of preliminary investigations into the manufacture of polyurethane coated cosmetic gloves with superior surface characteristics are reported.</p> <p>WRAMC FORM 0183 (ONE TIME) 15 MAY 1961</p>	<p>ABSTRACT CARD</p> <p>TITLE: Evaluation of a Series of Thermoplastic Polyurethane Elastomers</p> <p>AUTHOR(S): James C. Eaton, Jr.</p> <p>AGENCY: USA Prosthetics Res. Lab.</p> <p>Walter Reed AMC, Washington 12, D. C.</p> <p>TECH. RPT. 6309</p> <p>Project 6X59-01-001-04</p> <p>ABSTRACT: Physical properties and the resistance to attack by ultraviolet radiation and moisture have been determined for a series of thermoplastic polyester-urethane materials. Results of preliminary investigations into the manufacture of polyurethane coated cosmetic gloves with superior surface characteristics are reported.</p> <p>WRAMC FORM 0183 (ONE TIME) 15 MAY 1961</p>